学校编码：10384 密级______
学号：B200434016

厦门大学

博 士 学 位 论 文

珠江口有机物的组成、来源、分布和生物活性及其与缺氧的关系

Organic Matter in the Pearl River Estuary: its Composition, Source, Distribution, Bioactivity and their Linkage to Oxygen Depletion

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论文提交日期： 2010 年 10 月
论文答辩日期： 2010 年 11 月

2010 年 11 月

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A Dissertation Submitted to the Graduate School of Xiamen University

for the Degree of

Doctor of Philosophy

College of Oceanography and Environmental Science
Xiamen, Fujian

November 2010

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摘要

20 世纪 50 年代以来，有关近岸海域缺氧区的报道不断增多，已发展为全球性的重大生态环境问题。普遍认为，水体的层化和营养盐的大量输入引发的藻类过度繁殖是造成河口、近岸水体缺氧的主要原因。最新的研究认为河流输入的外源有机物可能是缺氧区耗氧有机物的另一种可能的来源。但是目前对河流输入的外源有机物和浮游植物自生的有机物在维持河口微生物呼吸作用的相对重要性还不清楚。

珠江是世界上最重要的20条大河之一，其流域地处典型的亚热带季风气候区，气温高，生物地球化学作用强烈。随着珠江三角洲地区经济的高速发展，人类活动已经严重影响了区域生态环境，近年来在珠江口上游观测到严重的表层水体缺氧现象。本论文针对珠江口缺氧问题，以有机物的来源、组成和生物活性为切入点，通过春、夏、秋、冬四个季节的现场观测和系统的过程研究，结合历史数据的集成分析，阐明了珠江口的缺氧区的时空变化规律；揭示了控制溶解氧(DO) 分布的主要因素；探讨了有机物的组成、来源、生物活性及其在河口的动态分布和调控机制；揭示了有机物降解和硝化作用与河口缺氧之间的关系。

研究发现，珠江口DO的分布呈现显著的空间差异和季节变化。从空间分布看，珠江口上游存在终年严重的全水柱缺氧现象，在广州后航道DO最低达2-9 μmol kg^{-1}，缺氧区一直延伸到虎门口附近，覆盖了~75 km的河道。虎门下游表层DO随盐度升高而明显升高，在外伶仃洋水域DO基本达到或略高于饱和浓度。从季节变化看，春季水体缺氧范围最广，缺氧程度最深，从虎门到广州后航道整条水道DO几乎都低于63 μmol kg^{-1} (即2 mg L^{-1})；夏季和秋季次之，表层DO也都低于100 μmol kg^{-1}；冬季缺氧程度较轻，虎门附近DO大约为200 μmol kg^{-1}。

统计分析表明，虎门上游表层DO与DOC、POC和NH_4^+的浓度呈显著的负相关，提示虎门上游有机物的有氧降解和硝化作用是导致水体缺氧的主要原因，冬季，河水与高DO的海水之间的混合也是控制表层DO分布的重要因素，并因此缓解了冬季虎门至狮子洋航道的缺氧程度。虎门下游表层DO主要受河、海水之间的混合以及水-气界面O_2的交换控制，但DOC、POC和NH_4^+浓度对DO的分布也有

重要的影响，其影响的程度因季节的不同而不同。河流的径流量对水体中DOC、POC和NH_4^+的浓度具有重要影响，进而显著影响河口的DO分布。

珠江口DOC的分布呈现显著的空间差异和季节变化，河口上游DOC的浓度明显高于下游，冬季和春季显著高于夏季。在珠江口上游，污水的输入是DOC的重要来源，特别是在径流量较小的春季，广州后航道污水输入对DOC的贡献高达54%，夏季较低为16%，说明径流对河口上游DOC的浓度有明显的稀释作用。珠江口DOC的生物可利用性较高，春季达15-45%，夏季为6-27%，这些活性DOC在河口传输过程中容易被生物降解。

在河口混合过程中，珠江口DOC表现出非保守混合行为，在低盐度区存在明显的去除。应用箱式模型计算得出，春季在河口上游DOC的去除通量为3.02×10^6 mol C d^{-1}夏季为6.86×10^6 mol C d^{-1}。群落呼吸作用和有机物的降解过程研究表明，微生物的有氧降解是决定河口上游DOC去除的主要途径，也是造成河口上游水体缺氧的主要原因之一。在主混合区(内伶仃洋)，DOC的行为表现出明显的季节差异。春季，DOC在主混合区仍有比较明显的去除，微生物降解是DOC去除的重要途径之一，占混合区DOC总去除的31%，此外还存在其它重要的生物地球化学过程控制DOC的去除。夏季，由于DOC的生物可利用性较低，河口水的停留时间短，DOC浓度在主混合区几乎没有变化。在河口下游DOC表观上呈现保守混合。

DOC的组分分析进一步揭示，在河口上游和主混合区，糖类和氨基酸被优先去除，而在河口下游，却存在多糖的添加。表明污水来源的活性DOC在河口上游和主混合区被优先降解，而在河口下游DOC表观上呈现的保守混合，是因为同时存在DOC的去除和添加。有机物的组成分析有助于深入认识河口DOC的生物地球化学变化过程。

POC的元素组成(C/N)和稳定碳同位素比值($\delta^{13}C$)显示，珠江口POC包括4种可能的来源：(1)淡水端浮游植物的生产；(2)河流输入的陆源颗粒物；(3)海水端浮游植物的生产；(4)污水的输入。结合POC/Chl-a的比值关系，以及河流输入POC的背景值，估算出珠江口上游，春季浮游植物对总POC的贡献的浓度加权平均值为42%，陆源POC的贡献为50%，污水的输入的贡献为8%。夏季浮游植物对总POC的贡献为26%，陆源POC的贡献为71%，污水的输入的贡献为3%。在主混合区，

浮游植物对POC的贡献比河口上游低，春季为31%，夏季为25%。在河口下游浮游植物对POC的贡献最高，其中春季为63%，夏季为32%。

珠江口POC浓度的分布呈现上游高下游低，冬、夏季较高，春、秋季节较低的分布特征。POC在珠江口上游存在快速去除，春季去除通量为5.92×10^6 mol d^{-1}，占河口上游总POC输入通量的68%，夏季去除通量为9.56×10^6 mol d^{-1}，为河口上游总POC输入通量的24%。微生物的有氧降解是决定河口上游POC去除的主要途径，也是造成河口上游水体缺氧的重要原因之一。

群落呼吸作用，硝化作用、浮游植物的光合作用和有机物耗氧降解等过程的研究表明，珠江口虎门上游缺氧区的形成主要是由于水柱的有机物有氧呼吸作用和硝化作用。氧收支模型计算表明，虎门上游缺氧区有机物有氧呼吸作用和硝化作用的耗氧通量相当，二者之和与水-气O_2的交换通量基本平衡，其它的生物和物理过程对缺氧区形成的贡献都是次要的。珠江口缺氧区的形成是生物、化学和物理过程耦合的结果。

本研究揭示了人类活动对河流输入的外源有机碳的来源、组成和活性的影响，强调了这些外源有机物对河口缺氧区形成的重要作用，为研究大河河口缺氧问题提供了新的视角，拓展了对世界大河河口缺氧机制的认识。

关键词：珠江口；缺氧；有机碳；有机物组分；稳定碳同位素组成；呼吸作用；硝化作用.

Abstract

There have been increasing reports pointing towards hypoxia in estuaries and coastal oceans since the 1950s, and it is therefore believed that hypoxia has become one of the most pressing global environmental issues. The formation of hypoxic zones in bottom waters has been commonly linked to high nutrient loads and water stratification. Alternatively, allochthonous organic matter may also contribute to the regional oxygen depletion. However, the role of allochthonous versus phytoplankton sourced organic matter in supporting microbial respiration throughout the hypoxic region is not well understood.

The Pearl River is one of the world's 20 largest rivers, the watershed of which is located in the typical sub-tropical monsoon climate area. With the rapid economic development and heavy urbanization in the Pearl River Delta, human activity has increasingly affected the regional environment in recent years. A very low DO concentration was observed in the surface water in the upper reach of the Pearl River Estuary. This dissertation is examining the processes associated with the formation and the maintaining of oxygen depletion zones in the Pearl River Estuary. Emphesis is given to the sources and bioactivity of organic matter, and its linkage with the oxygen depletion in this region. This study is based on the date collected from four seasons during 2004-2008 in the Pearl River Estuary; the previous observation data were also assembled to identify the spatial and temporal variability of hypoxia in the Pearl River Estuary.

Significant spatial and seasonal variations of surface DO concentration were observed in the Pearl River Estuary. Oxygen depletion in the water column existed in the upper reach of the Pearl River Estuary or upstream Humen throughout the year. This oxygen depleted zone extended from Humen to the suburbs of Guangzhou, covering ~75 km water body, with a lowest surface DO concentration of 2-9 μmol O_2 kg^{-1} near Guangzhou. Downstream the Humen Outlet, surface DO concentration increased with salinity, reaching almost saturation or supersaturation in the lower

estuary. Seasonally, the most oxygen depleted season was observed in spring, followed by the summer and autumn, and winter.

Statistical analysis showed that surface DO concentration in the upper reach was mainly correlated with DOC, POC and NH_4^+ concentrations. In winter, estuarine mixing only played a significant role in bringing up oxygen content in the water upstream Humen. Downstream Humen Outlet, surface DO concentration was mainly controlled by water mixing throughout the year while the impacts of DOC, POC and NH_4^+ contents were different depending on the season.

Significant spatial and seasonal variations of DOC and its major compouds were observed in the Pearl River Estuary. The concentrations of DOC and its major compounds, carbohydrates and amino acids, were high in the upper reach of the Pearl River Estuary and decreased rapidly downstream. In terms of seasonality, a significantly higher DOC was observed in winter than that in summer. Anthropogenic sewage input appeared to be an important source of the DOC pool in the upper reach. The contribution of anthropogenic sewage input to total DOC was accounted for ~54% in the upper reach in spring (dry season), and ~16% in summer (wet season), indicating that the sewage-derived DOC in the upper reach was sharply diluted by the river discharge. The biodegradable DOC (BDOC) was relatively high in the Pearl River Estuary, with a range of 15-45% in spring and 6-27% in summer. This portion of DOC was easily degraded during the transport through the estuary.

DOC distribution was non-conservative during the estuarine mixing, showing a net consumption of DOC in the upper reach and in the low salinity region of the Pearl River estuary. The removal fluxes of DOC in the upper reach were 3.02×10^6 mol C d^{-1} in spring and 6.86×10^6 mol C d^{-1} in summer. Community respiration and DOC consumption incubations showed that microbial degradation was the major process controlling the DOC removal in the upper reach. This heterotrophic biodegradation of organic matter was one of the most important processes controlling the severe oxygen depletion in the upper estuary. In the mixing zone, the distribution of DOC showed significantly seasonal variability. In spring, microbial degradation was recognized as

one of important processes controlling the behavior of DOC, which accounted for ~31% of total DOC removal. Other processes were also important reasonable for DOC removal. While in summer, DOC concentration was almost constant in the mixing zone. In the lower estuary, the heterotrophic removal almost balanced by the autotrophic production resulting in a linear distribution of DOC with salinity.

Organic composition analysis showed that the major compounds of DOC changed rapidly along the estuary, showing a selected removal of carbohydrates and amino acids within the DOC pool in the upper reach and mixing zone and an autotrophic source of PCHO in the lower estuary.

Elemental (C/N) and bulk organic carbon isotope composition ($\delta^{13}C$) of particulate organic carbon (POC) showed that there were four potential sources of organic matter in the POC pool: (1) fresh water phytoplankton production, (2) terrestrial organic matter, (3) marine phytoplankton production, and (4) wastewater input. A combination with the POC/Chl-a ratios of the phytoplankton and the background values of river-derived terrestrial POC concentration allowed for an estimation of the contribution of the phytoplankton biomass to POC as ~42%, the land-derived POC as 50%, and wastewater input as ~8% during the spring season. The contribution of the phytoplankton biomass to POC was estimated as ~26%, the land-derived POC as 71%, and wastewater input as ~3% during summer season in the upper reach the Pearl River estuary. The contribution of phytoplankton biomass to POC decreased along the estuary to a value of ~31% in spring and ~25% in winter in the mixing zone, and then enhanced in the lower estuary to a value of ~65% in spring and ~32% in summer.

The distribution of POC in the Pearl River Estuary showed large spatial and seasonal variability. High POC concentrations were observed in the upper reach and decreased rapidly downward. The distribution of POC was mainly controlled by river discharge, with higher POC concentrations in winter and summer and the lower concentrations in spring and autumn. A significant removal of POC was observed in the upper reach of the estuary. The removal flux was 5.92×10^{6} mol C d^{-1}, accounting for 68% of POC input in spring, and 9.56×10^{6} mol C d^{-1}, accounting for 24% POC

input in summer. Microbial degradation was the major process controlling the POC removal in the upper reach. This heterotrophic biodegradation of POC was another important process controlling the severe oxygen depletion in the upper estuary.

Both the respiration of organic carbon and nitrification were main processes which controlled oxygen depletion in the upper reach of the Pearl River Estuary. Oxygen budget calculations showed that the consumption of oxygen by respiration and by nitrification was nearly equal, and the sum was balanced by the reaeration process. Contributions from other processes such as phytoplankton photosynthesis, and sediment oxygen demand were marginal.

This dissertation revealed the impact of anthropogenic activities on the source and fate of river-derived organic matter, and emphasized the important of allochthonous organic matter in forming and maintaining the oxygen depletion in the estuary.

Keywords: Pearl River Estuary, oxygen depletion, organic carbon, organic matter composition, organic carbon isotope composition, respiration, nitrification.

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